6.01 Diagnostic Evaluation of Carbon Sources in CMAQ

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Abstract   Traditional monitoring networks measure only total elemental carbon (EC) and organic carbon (OC) routinely. Diagnosing model biases with such limited information is difficult. Measurements of organic tracer compounds have recently become available and allow for more detailed diagnostic evaluation of CMAQ modeling results, which allow for more explicit representation of secondary organic aerosols. An enhanced version of the model makes it possible to track contributions from various sources of primary organic aerosols and elemental carbon, providing more in-depth evaluation of model biases. An ambient $PM_{2.5}$ measurement campaign conducted in four Midwestern U.S. cities in March 2004 February 2005 allows for direct comparison of modeled and measured organic carbon concentrations by primary and secondary source category.

Keywords: **CMAQ, air quality modeling, diagnostic model evaluation, elemental carbon, organic carbon, organic tracer**

1. Introduction

Routine monitoring networks measure only total elemental carbon (TEC) and total organic carbon (TOC). These measurements are useful to ascertain how an air quality model performs in predicting

these quantities and have been used for this purpose in the past (Carlton et al., 2010; Foley et al., 2010). However, it is difficult to diagnose model biases with such limited data. Instead, specialized measurement campaigns are necessary.

One such specialized measurement campaign was conducted in the midwestern United States between March 2004 and February 2005. During this time, data was collected at four sites in the region: Bondville, IL; Northbrook, IL; Cincinnati, OH; and Detroit, MI. At each site, over 80 particle-phase organic compounds, including alkanes, hopanes, steranes, organic acids were measured on filters sampled every 6th day. The filter extracts were composited on a monthly basis and analyzed by chemical derivatization and gas chromatography. The composites were also analyzed by EPA scientists for highly polar compounds, which are known tracers of secondary organic aerosol (SOA) production (Lewandowski, et al. 2008).

In this study, the tracer measurements were compared to modeling results obtained from a simulation over the entire episode using a version of the CMAQ model outfitted with the ability to track 16 individual sources of primary EC and OC. This version of the model also included the recent enhancement to the SOA module allowing for a complete comparison with the measured tracer compounds.

2. Method

At first a traditional evaluation of total carbon (TC) was performed for the four sites listed above. While model performance varied in time, five scenarios of interest emerged.

(1) Small (-0.3 ug/m^3) bias was recorded in the spring months in Detroit.
(2) Large (-1.0 ug/m^3) bias was recorded in the spring months in the three other cities.
(3) Large (-1.7 ug/m^3) bias was recorded in the summer months at all four sites.
(4) Large (-1.4 ug/m^3) bias was recorded in the winter months at Northbrook.

(5) Small (-0.2 ug/m^3) bias was recorded in the winter months in the three other cities.

To explain the sources of these biases, the CMAQ model was modified to keep track of 16 different categories of EC and OC including on road diesel exhaust, coal combustion, nonroad diesel exhaust, oil combustion, on road gasoline exhaust, natural gas combustion, nonroad gasoline exhaust, food cooking, aircraft exhaust, paved road dust, anthropogenic biomass combustion, crustal material, wildfires, misc. industrial processes, waste combustion, and other. The resulting source specific EC and OC modeled concentrations were paired with laboratory determined source profiles to transform TC concentrations to predictions of the measured organic tracers according to the following:

$$[Tracer]_i = \sum_j Profile_{i,j}[C]_j, \qquad (1)$$

where $[Tracer]_i$ is the concentration of a measured organic tracer i, $[C]_j$ is the TC concentration from source j, and $Profile_{i,j}$ is the laboratory measured profile of tracer i from source j. An example of source profiles for butanedioic acid and Perylene appears in Figure 1.
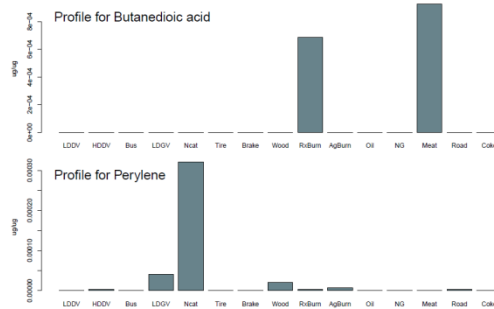

Figure 1. Source profiles for two organic tracers. Butanedioic acid (above) originates mainly from prescribed burning and meat cooking, while Peryle (below) ne originates mainly from mobile sources.

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3. Results and Discussion

Several categories of emissions were analyzed to discern possible sources of biases in the emissions of EC and OC. Among these, it was found the model performed relatively well at simulating TC emissions from mobile sources at all sites, which were characterized by measurements of hopanes and steranes. Sources of biomass combustion, characterized by measurements of levoglucosan, were found to explain the negative summer-time bias at all of the sites. Production of secondary organic aerosol characterized by model predictions of isoprenes, monoterpenes, sesquiterpenes, and aromatics was also a source of large bias throughout the year. The good TC model performance during the spring in Detroit was found to be caused by compensating errors, where overestimation in emissions from burning natural gas were found to offset TC sources from other categories. The five cases of interest identified above were found to be influenced by biases in the emissions categories according to Table 1, which can be used to guide further model development efforts in order to improve prediction of TC concentrations.

*all quantities in µgC/m^3	Spring (Mar, Apr, May)		Summer (Jun, Jul, Aug)		Winter (Nov, Dec, Jan,
	Detroit	Non-Detroit	All Cities	Northbrook	Non-Northbrook
TC Bias	-0.3	-1.0	-1.7	-1.4	-0.2
Mobile	0.1	0.2	0.1	0.1	0.0
Natural Gas	-0.2	-0.0	-0.0	-0.0	-0.1
Biomass	-0.1	0.1	0.4	0.3	0.1
α-pinene SOA	0.2	0.1	0.3	0.0	0.1
Aromatic SOA	0.2	0.1	0.2	0.0	0.0
Isoprene SOA	0.1	0.2	0.7	-0.0	0.0
β-caryophyllene SOA	0.3	0.1	0.1	0.2	0.2

References

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Questions and Answers

Questioner Name: D. Simpson

Q: In European source-apportionment efforts, we have used typically 14C, levoglucosan, etc. to test models. We have also used similar SOA tracers as was shown here, but found large differences. More work is needed on these issues.

A: This type of comparison is limited mostly by measurement data availability. I agree that more work is needed on these issues, and to accomplish that, stronger collaborations are needed between modelers and the measurement community. Also, it would be interesting to apply our techniques to the European data.

Questioner Name: C. Fountoukis

Q: Would using high time resolution measurements give more inside information about model bias?

A: It is unlikely that higher time resolution would give any additional information for a comparison such as this, because the organic tracers are measured in extremely small quantities already and require longer composite sampling.

Questioner Name: S. Aksoyoglu

Q: Comment about missing b-caryophyllene in winter: it seems that some terpenes are released when trees are cut and burned in winter. This might be one of the missing sources.

A: We are currently pursuing a related effort focused specifically on biomass combustion emissions. We appreciate this comment and will definitely investigate further.